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ABSTRACT

Halogenated organic solvents are of particular concern in closed atmospheric situations such as nuclear submarines, spacecraft, and hyperbaric chambers due to their corrosive and toxic potential. A gas chromatographic on-column concentrating technique has been developed for the analysis of halocarbons in atmospheric gas mixtures, thus eliminating the use of cold traps. An important part of this analytical system is a coulometric detector which is specific for chlorinated, brominated, or iodated hydrocarbons. By making use of this specific detector and the on-column concentrating technique, gas samples can be analyzed quantitatively for chlorinated contaminant compounds at concentrations as low as 10 to 20 parts per billion by volume.

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DETERMINATION OF TRACE QUANTITIES OF HALOGENATED HYDROCARBONS IN GAS SAMPLES

INTRODUCTION

The industrial and commercial usage of volatile halogenated hydrocarbons, particularly in the C_1 to C_3 range, has greatly increased in recent years. These compounds are commonly used in many products and processes today, and consequently we can expect to find them in closed atmospheres such as in nuclear submarines, spacecraft, and hyperbaric chambers. Chlorinated hydrocarbons, for example, are often used to give flammability resistance to solvent formulations. In addition they are inherently good solvents for polymers and other organic materials. Chlorofluorocarbons are in common use as refrigerants, aerosol propellants, fire extinguishing agents, degreasers, cleaners, and general solvents. In addition, a few bromofluorocarbons are in general use.

Halogenated organic solvents are of particular concern in closed atmospheric situations because of their potential contribution to corrosion problems, deterioration of organic materials, and relatively high toxicity. In addition, halogenated hydrocarbons will decompose under some conditions to yield compounds of greater toxicity and corrosivity than the parent compounds (1,2). Consequently, it is important to control and remove these compounds from closed atmospheres. The first step needed to accomplish this is a good analytical method which can be used to identify and determine the quantitative distribution of halogenated hydrocarbons in gas samples of these atmospheres. Compounds containing chlorine are of particular interest because of their common occurrence.

Because of the large number of contaminant compounds of all kinds found in many closed atmospheres, extensive interference can be expected when it is desired to determine the concentrations of any particular compounds. The difficulties are compounded because of the very low concentration of each compound. In the past, special techniques have been used to separate out certain types of compounds, followed by detailed analyses for individual compounds. Such techniques were used in the determination of aromatic hydrocarbons in nuclear submarines, by concentration of the organic contaminants on activated carbon with subsequent desorption and analysis in the laboratory (3).

It would be much more desirable to make analyses for trace organic compounds on gas samples directly, or on compressed atmosphere samples taken in the closed environment in order to avoid the problems which occur when an onsite concentration step is used. As an example of such problems, adsorption of organic compounds from closed atmospheres on activated carbon, followed by desorption for analysis in the laboratory has been a powerful tool for learning what compounds are present. However, the data obtained are often considered semiquantitative at best and sometimes only a qualitative indication of the compounds in the atmosphere (4).

Since identification of specific compounds present in a given atmosphere and determination of their concentrations are very difficult, because of the many hundreds of individual compounds and the very low concentrations of each compound usually found, gas chromatography is especially useful with its enormous power for separating individual compounds in the separation column. It would be much more powerful if the detector unit of the gas chromatograph could be used as a second screening tool. In other words, if the

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detector responded only to certain types of molecules of interest and ignored all the rest, identification of a given peak would be more certain and its quantification made easier.

Since the advent of gas chromatography as an analytical tool, the development of detectors for organic compounds has proceeded in two principal directions, high sensitivity and high specificity. Some detectors have been developed which have very high sensitivity, such as the flame ionization detector which can detect most hydrocarbons down to the parts per billion range. This detector is not discriminatory, however, because it will respond to almost all organic compounds, although with somewhat lesser sensitivity to those containing a high proportion of halogens.

The electron capture detector is largely discriminatory, being very sensitive to highly electronegative compounds. However, the variation of sensitivity to compounds of the same class covers many orders of magnitude. For example, the signal this detector gives for carbon tetrachloride is 7000 times as large as the response for chlorobenzene (5). Another disadvantage of the electron capture detector is that it is sensitive to nonhalogen compounds such as some unsaturated dibasic esters, unsaturated aromatic hydrocarbons, aromatic aldehydes, and nitro aromatic compounds. Other disadvantages are the need for separate calibration factors for each compound, nonlinearity of response, and detector instability. Most of these factors increase the difficulty of achieving quantitative results.

The development of the coulometric detector, which employs a highly specific titration cell to respond to certain atoms, is another highly significant development. For example, one such commercially available unit, operating in a certain mode, responds only to chlorine, bromine, and iodine atoms (6,7). Although not having as high an ultimate sensitivity as some other methods, the coulometric detector responds only to compounds containing these halogen atoms and completely ignores hydrocarbons and other nonhalogenated compounds. For this reason the microcoulometric detector was chosen for the difficult assignment of detecting and analyzing the concentrations of the halogenated compounds in the complex gas mixtures which comprise the atmospheres of submarines and other closed environments. The lesser sensitivity was compensated for by special techniques described in this report.

APPARATUS AND STANDARDS

The chromatograph used was a Microtek MT-220 equipped with a Dohrmann microcoulometer and a multifunction programmer. An F&M model 810 chromatograph equipped with an electron capture detector was used to compare the electron capture response to the microcoulometer's response. The column packing materials used in the on-column concentrating technique were Porapak Q and S, obtained from Waters Associates, Inc.

The chlorinated and brominated hydrocarbon standards were prepared in 1.7-liter gas bottles made of stainless steel, and obtained from Alloy Products Corp. The fluorocarbons were obtained from the Du Pont Co., and the other halogenated hydrocarbons were purchased from Chem Service, Inc.

The gas mixtures were prepared by dilution techniques. In the case of liquid halogenated compounds, a calculated volume of the liquid was injected with a microsyringe, through a septum, into an evacuated gas bottle, which was then pressurized to 300 psia with air or helium. For lower concentrations of these compounds, aliquots of the original mixtures were diluted further.

DEVELOPMENT OF THE METHOD

The Dohrmann microcoulometric detector, with a silver cell and operating in the oxidative mode, is specific for halide ions, except for fluorides. As the halocarbon components of the mixture are eluted from the chromatographic column they are pyrolyzed in an oxygen stream at 950°C, thus rendering the halogen titratable with silver ions. The coulometric analysis is of particular value since the response of the detector, when related through Coulomb's law, is an absolute quantitative measure of the chloride ions present. This makes it unnecessary to precalibrate the detector for various compounds as long as combustion is complete. Since the response of the detector is determined by the number of chloride atoms in the molecule, there is not a large difference in response factors between various compounds as is the case with the electron capture detector. Thus the problem of one compound overwhelming another due to great differences in response factors does not occur with the coulometric detector.

The real utility of the microcoulometric detector is demonstrated by the chromatograms in Fig. 1, which illustrate the specificity of the detector to the halogenated compounds in practical mixtures. In this case a gas sample taken in a closed atmosphere was injected into the chromatograph. After passing through the separation column, the effluent gas stream was split, with a small portion of the carrier gas going to a flame ionization detector and the rest of the carrier gas going to the microcoulometric detector, the two detectors feeding into a single two-pen recorder. The flame detector responds to almost any organic compound present in the atmosphere, as shown in the upper chromatogram in Fig. 1. The microcoulometer, or lower, chromatogram is much simplified because this detector responds only to the chlorinated compounds in the mixture and ignores all the other compounds. Note, for example, that the first six peaks are absent. The peaks in the microcoulometer trace are clean and symmetrical, whereas the asymmetry in the peaks of the flame, or upper, chromatogram suggests the presence of even more compounds than are enumerated.

It may be noted also that the baseline of the flame chromatogram changes due to degradation of the polymeric column packing as the temperature is raised during the development of the chromatogram. The microcoulometer does not respond to the degradation products since they do not contain halogen atoms.

The dynamic range of sensitivity for the microcoulometer is reported (6) to be from 0.1 to 1000 mg of chloride ions. In the present work, the desired limits of detection of halogenated hydrocarbons for trace analysis were in the range of ten parts per billion (ppb) to ten parts per million (ppm) by volume.

A concentrating technique was required to achieve these desired detection limits with the coulometric detector. It had been previously observed by Hollis (8) that the gas chromatographic retention times of hydrocarbons and halogenated hydrocarbons are quite long and varied on porous polyaromatic polymer bead (Porapak) columns as compared to normal gas liquid chromatographic (GLC) columns. The good separation possible with the Porapak column helps eliminate one of the disadvantages of the coulometer, i.e., slow response, so there would not be interference of one peak with the next.

A particularly unique advantage can be realized by the use of porous polymer beads, in that at room temperature even the lower molecular weight halogenated hydrocarbons have a very long retention time. In fact, it was found that even the more volatile contaminants in air samples could be concentrated on the Porapak column at room temperature. The halogenated contaminants apparently remain concentrated in a very narrow zone at the head of the column until the column temperature is increased, which permits the elution of symmetrical peaks. Atmosphere samples as large as 500 ml have been concentrated on a porous polymer column at 50°C. A detailed discussion of this on-column concentrating technique is given in Ref. 9.
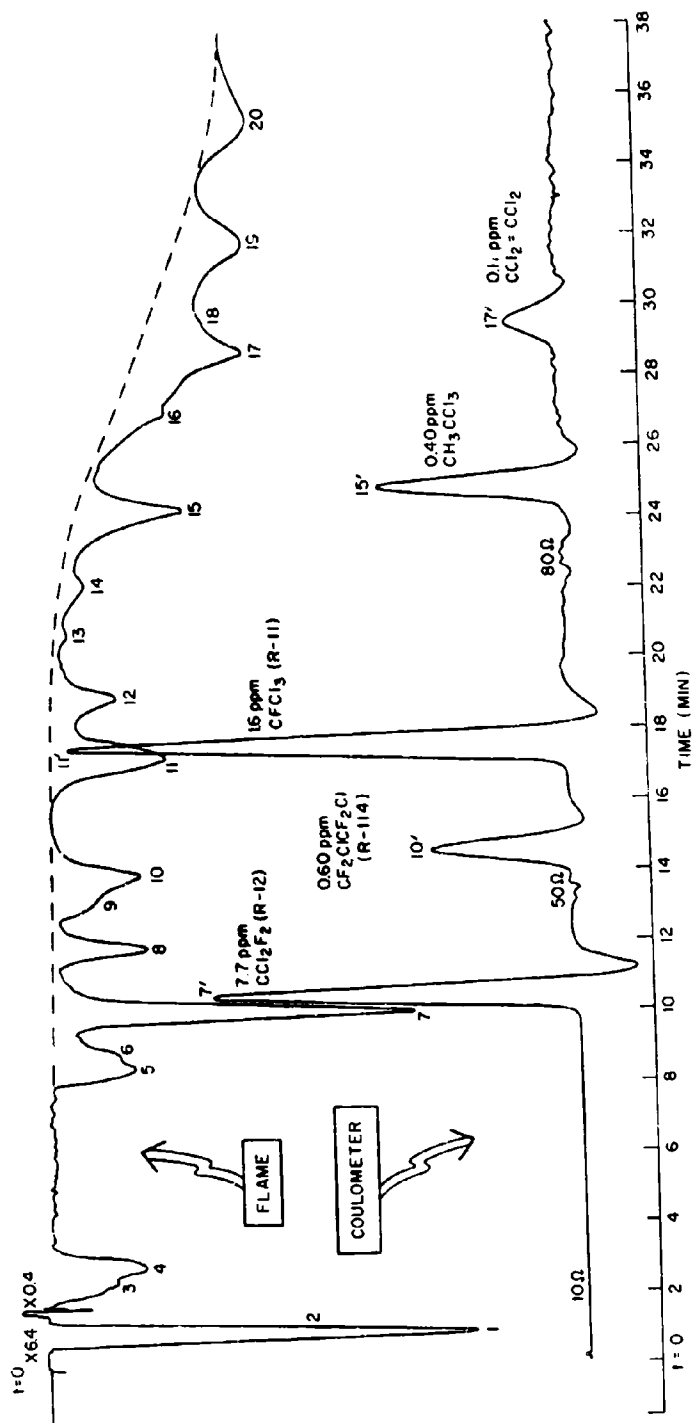
Fig. 1 – Simultaneous chromatograms of an atmosphere by hydrogen flame and microcoulometer detectors

An important tool employed in the development of the analytical method was multiple-step temperature programming, which within a reasonable time permitted the analysis of chlorinated compounds in a wide boiling range. The molecular weights of the halogenated hydrocarbons of interest varied over a wide range, so that under isothermal column conditions the retention times on porous polymer beads ranged over several hours. In order to obtain a sharp resolution of each component, special temperature programming was necessary. This allowed the analysis of such compounds as CF_2Cl_2 (bp -30°C) and $CCl_2=CCl_2$ (bp 121°C) on the same run, and produced sharply peaked results in a reasonable time. At the initial temperature, 30 to 50°C, the halogenated compounds are trapped at the head of the separation column. Following this step, the compounds of interest are eluted and separated by using an appropriate temperature program. The type of Porapak and the particular temperature program that is used depends on the mixture to be analyzed. Such a program is illustrated in the typical analytical procedure described in the next section.

Care must be taken to eliminate adsorption in the sample loop and sample valve when working with trace contaminants. Due to the high volatility of the compounds analyzed and the fact that a sufficient volume of carrier gas was used to inject the samples, there was not, in the present work, any appreciable loss due to adsorption of the chlorinated hydrocarbons studied.

TYPICAL ANALYTICAL PROCEDURE

A procedure that has been used successfully for a number of submarine atmosphere samples is as follows:

A portion of the gas sample to be analyzed is put in a 100 or 500 ml sample loop. Care is taken to equilibrate the column oven at a selected temperature between 30 and 50°C, in this case 50°C. This equilibrium temperature must be the same for each analysis, or the retention times of the sample components will vary slightly in repetitive runs. The sample valve is opened and the sample moved by the helium carrier gas from the sample loop onto the column over a 5-minute period. The flow rate of the carrier gas must be high enough to transfer the sample from the loop to the column in the allotted time. The organic contaminants are eluted from the column by raising the temperature according to the temperature program shown in Fig. 2. After the 5-minute sample sweep by the carrier gas at 50°C, the temperature is raised at the maximum heating rate to 100°C and held at this temperature for 5 minutes. The temperature is then raised to 215°C in three steps. After holding at 215°C for 12 minutes, the column oven is cooled at the maximum rate to bring the oven temperature back to 50°C and allowed to equilibrate there for 10 minutes in preparation for injection of the next sample.

To clean the Porapak column of higher molecular weight compounds that are present in the submarine samples, the temperature of the column is held at 210°C overnight, with some helium carrier gas flowing to flush the column. An alternate method of stripping the column would be to backflush. Stripping the column is necessary in order to have the retention times of individual compounds remain constant from day to day.

DISCUSSION

By following a procedure such as the one described, many halocarbons commonly encountered can be separated and identified as discrete peaks. Table 1 lists the compounds studied and their boiling points, which cover a range from -81 to 132°C. By careful selection of the temperature program, all of these compounds have been separated and recorded as discrete peaks at concentrations as low as 10 ppb by volume in

Table 1
Halogenated Hydrocarbons Analyzed by
Microcoulometric Gas Chromatography

| Compound	Formula	BP (°C)
Chlorotrifluoromethane	CF_3Cl	-81.4
Bromotrifluoromethane	CF_3Br	-57.8
Chloropentafluoroethane	CF_3CF_2Cl	-38.7
Chlorodifluoromethane	CF_2ClH	-40.8
Dichlorodifluoromethane	CCl_2F_2	-29.8
Chloroethene	$CH_2{=}CHCl$	-13.9
1,2-Dichloro-1,1,2,2-tetrafluoroethane	CF_2ClCF_2Cl	3.8
Dichlorofluoromethane	CCl_2FH	8.9
Trichlorofluoromethane	CCl_3F	23.7
1,1-Dichloroethene	$CH_2{=}CCl_2$	37
cis-Dichloroethene	$CHCl{=}CHCl$	60
1,1,2-Trichloro-1,2,2-trifluoroethane	CCl_2FCClF_2	47.6
trans-Dichloroethene	$CHCl{=}CHCl$	48.3
1,1,2,2-Tetrafluoro-1,2-dibromoethane	CF_2BrCF_2Br	47.3
Trichloromethane	$CHCl_3$	61.2
1,2-Dichloroethane	CH_2ClCH_2Cl	83.5
1,1,1-Trichloroethane	CH_3CCl_3	74.0
Trichloroethene	$CCl_2{=}CHCl$	87.2
1,1,2-Trichloroethane	$CHCl_2CH_2Cl$	113.5
Tetrachloroethene	$CCl_2{=}CCl_2$	121.2
Chlorobenzene	C_6H_5Cl	132
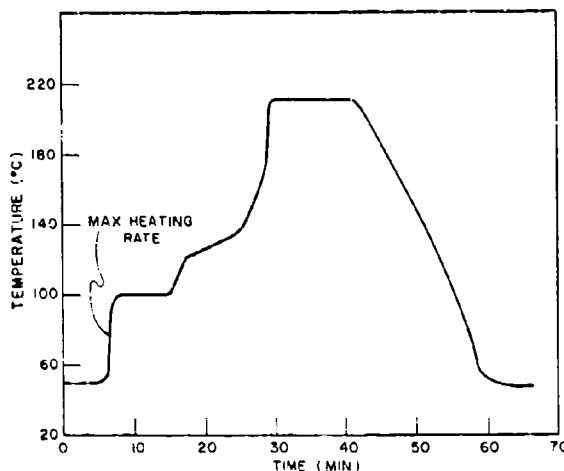
Fig. 2 – A typical temperature program

air samples. These separations are shown in Fig. 3 in a line chromatogram, with the vertical lines indicating the retention times of each compound.

Just as in the case of many other analytical techniques, certain characteristics are inherent to this method and should be understood for best results. These peculiarities are perhaps best explained by examining some actual chromatograms. For example, in Fig. 4 an overshoot below the baseline, followed by recovery to the baseline, is seen to occur. For quantitative analysis, it is necessary to subtract the area of the overshoot from the area of the peak, to get the true area for the chloride ions. The appendix gives an example of the method used for calculating concentration from peaks in the chromatograms.

A second unique phenomenon observed with the coulometric detector for chloride is also illustrated in Fig. 4. The peak which appears badly misshapen, can be a quantitative representation of the amount of chlorine compound under the peak. The response of the microcoulometer is somewhat different from other chromatographic detectors in that a peak may appear to be flat at its maximum, but the area is still a direct quantitative measure of the chloride ions present.

Quite frequently a practical atmospheric sample will contain a component at a very high concentration relative to other components, Fig. 5 a case in point. Peak 2 was identified as dichlorodifluoromethane, $CCl_2 F_2$, which is a common refrigeration gas, R-12. With a peak as broad as Peak 2, there is no way to tell what other chlorinated compounds may be hidden in it. A technique was developed in which the large interfering peak could be vented after the separation column so that it did not pass through the detector, then the effluent was allowed to enter the detector again in a search for other compounds. This procedure was followed with this sample, and the chromatogram obtained is shown in Fig. 6. The R-12 peak was eliminated and the new Peak 2, which has a longer retention time, was identified as R-114, $CClF_2 - CClF_2$.
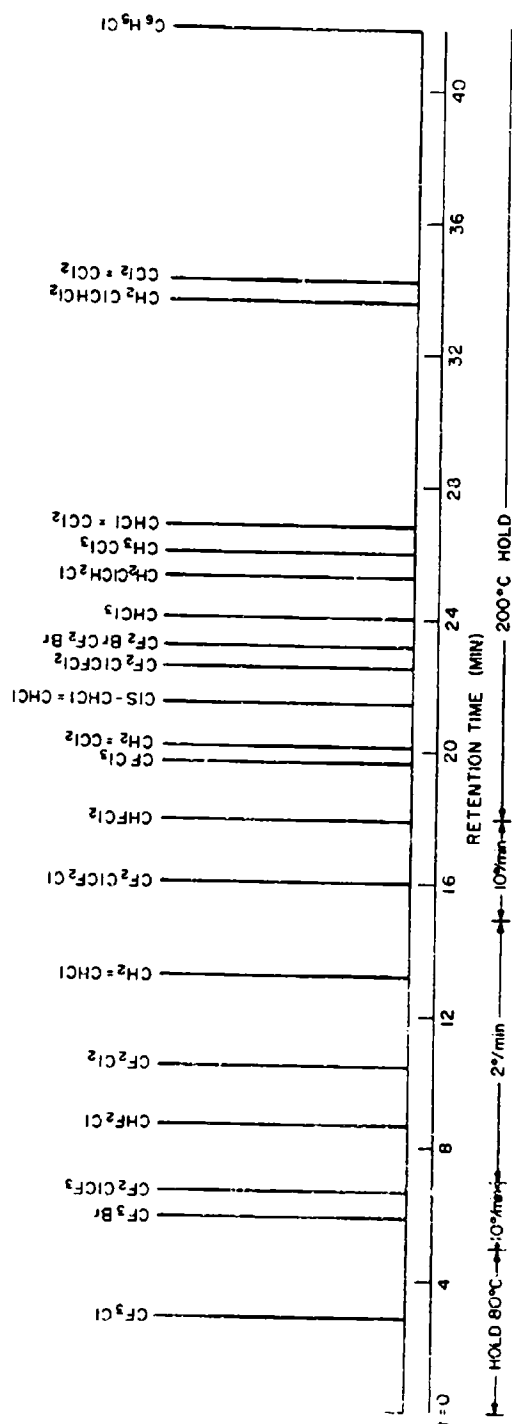
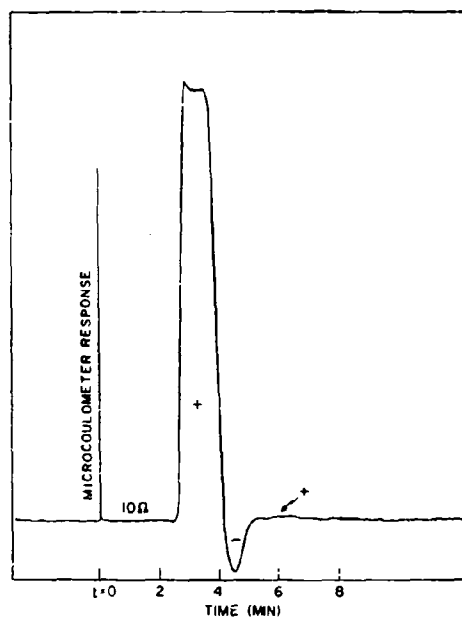Fig. 3 — Retention times of chlorinated compounds

Fig. 4 - Microcoulometric response
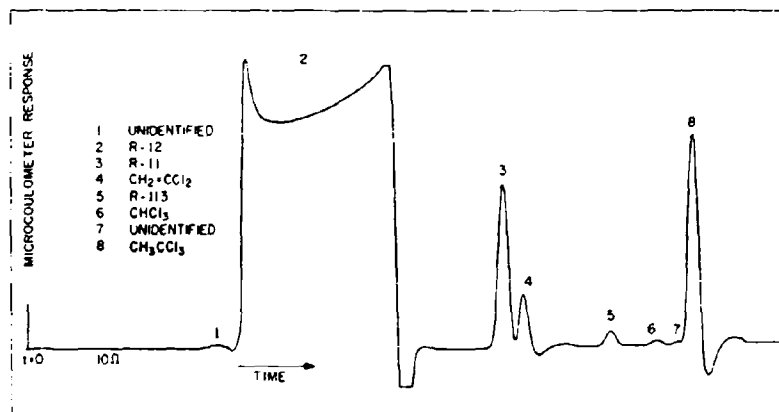obtained from an overloaded cell

Fig. 5 - Chromatogram of atmosphere
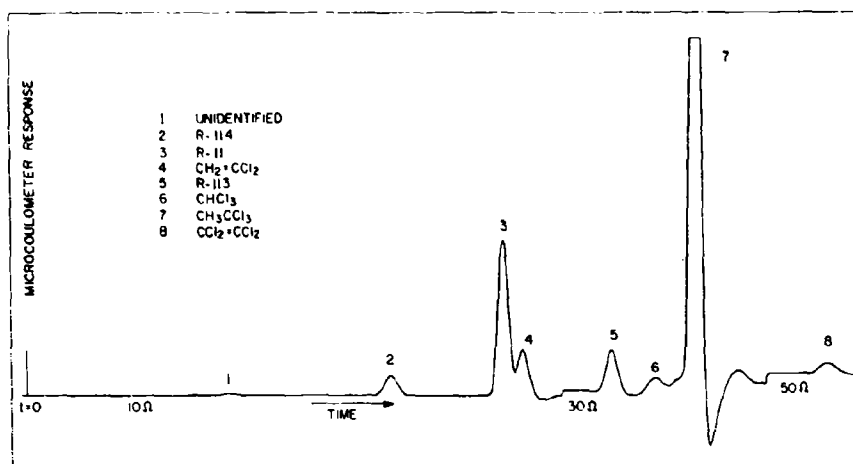sample with large peak

Fig. 6 – Chromatogram of atmosphere
sample with large peak vented

Up to now, the discussion has dealt with compounds containing chlorine. However, the coulometric detector is also useful for detecting bromine compounds, but as yet such compounds are not nearly as common as chlorine compounds. For quantitative work it is necessary to calibrate the instrument carefully for each bromine compound, because a fraction of the bromine atoms appears in the titration cell as hypobromite ions, which are not precipitated by silver ions. In the present work, this detector has not been tried for compounds containing iodine, although it is reported to respond to them also (6).

CONCLUSIONS

The analytical techniques described here have been very useful at NRL for studying trace contaminants in atmospheres of closed environmental systems, gas samples from many sources, and product mixtures from studies of chemical reactions.

It has been demonstrated that a chromatographic detector specific for certain elements can be used to great advantage for analyzing gaseous or liquid mixtures. The on-column concentration on Porapak eliminated the use of cold traps and enhanced the sensitivity of the microcoulometer so that gas samples could be analyzed quantitatively for chlorinated contaminant compounds at concentrations as low as 10 to 20 parts per billion by volume. In the case of the microcoulometer with a silver cell operating in the oxidative mode, a quantitative picture of the chlorinated hydrocarbon compounds present can be obtained without the confusion of the other compounds in the total mixture.

The microcoulometric detector has two unique characteristics. From a qualitative standpoint, the microcoulometer greatly narrows the number of possible compounds to be considered. At the same time, the output of the microcoulometer is a direct quantitative measure of the chlorinated hydrocarbons present.

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Appendix

METHOD OF CALCULATION OF CONCENTRATION OF A COMPONENT
IN A SAMPLE FROM A PEAK ON A CHROMATOGRAM

The numerical values for the components in a mixture are usually expressed in parts per million (ppm) by volume or micrograms per liter ($\mu g/1$).

The equation for the calculation of the volume of a particular component in a mixture at one atmosphere pressure is given as

$$V_i = \frac{ASqRT}{MrCFP} \times 10^2,$$ (1)

where

V_i = volume of components, liters;

A = peak area, in.^{2};

S = recorder sensitivity, sec/in. $\times$ V/in.;

q = equivalent weight of chlorine, g/eq;

R = gas constant, 0.08205 1-atm/$^{\circ}$K-mole;

T = absolute temperature of gas sample, $^{\circ}$K;

M = molecular weight of compound, g/mole;

r = recorder input resistance, ohms;

C = percent chlorine in compound, %;

F = Faraday constant, 96,500 coulombs/eq;

P = pressure of gas sample in gas sample loop, atmospheres.

The following equation converts V_i, Eq. (1), to parts per million by volume:

$$ppm = \frac{V_i}{V_T} \times 10^6,$$ (2)

where

V_T = total volume of the mixture, liters.

A sample calculation for the CCl_2F_2 (R-12) peak in Fig. 1 is as follows:

Peak area = + 1.38 in.^{2} (taken when sample was at 298°K)

            − 0.21 in.^{2} (corrections for overshoots below the baseline)

            + 0.02 in.^{2} (corrections for overshoots above the baseline)

              1.19 in.^{2}

$$V_i = 10^2 \frac{(1.19 \text{ in.}^2)[(120 \text{ sec/in.})(1.06 \times 10^4 \text{ V/in.})]}{(12 \ .95 \text{ g/mole})(10\Omega)(58.6\%)} \times (35.5 \text{ g/eq})(0.0820 \text{ 1-atm/°K-mole})(298°K) \atop \times (96{,}500 \text{ coulombs/eq})(1 \text{ atm})$$

$$= 0.192 \times 10^{-6} \text{ liters}$$

$$ppm_{R-12} = \frac{V_i}{V_T} \times 10^6 = \frac{0.192 \times 10^{-6}}{0.025} \times 10^6$$

$$= 7.7$$

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Naval Research Laboratory Washington, D.C. 20390	Unclassified
	2b. GROUP

3. REPORT TITLE

DETERMINATION OF TRACE QUANTITIES OF HALOGENATED HYDROCARBONS
IN GAS SAMPLES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

An interim report on a continuing problem.

5. AUTHOR(S) (First name, middle initial, last name)

Frederick W. Williams, Merle E. Umstead, and J. Enoch Johnson

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
November 6, 1969	18	9

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
NRL Problems C08-30 and C08-33	
b. PROJECT NO. SF35-433-002-13215, 13213 and	NRL Report 6964
c. S4607-11897	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Department of the Navy (Naval Ship Systems Command), Washington, D.C. 20360

13. ABSTRACT

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1 NOV 65

S/N 0101-807-6801

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Coulometry						
Gas chromatograph						
Halohydrocarbons						
Trace analysis						
Chlorocarbons						
Trace contaminants						

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